RAMAN SPECTROSCOPIC STUDIES OF FUSED SALT ELECTROLYSIS

Donald R. Sadoway

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts   02139
. U.S.A.

INTRODUCTION

Fused salt electrolysis is used both in the primary extraction of metals from their ores (electrowinning and electrorefining) and in the generation of coatings (electroplating). Extraction by fused salt electrolysis is a very energy-intensive process. The production of primary aluminum and magnesium is estimated to have consumed 2.1% of total generated electric power in the United States during the year 1985 (1). Accordingly, research has been directed at reducing energy consumption in electrowinning. Coatings made by fused salt electroplating are typically rough or dendritic, but rarely smooth. Thus, research has been directed at improving surface finish and deposit morphology.

The purpose of this article is to describe the use of Raman spectroscopy in addressing the issues raised above and in attempting to achieve the related research objectives. In principle, Raman spectroscopy has the capability to analyze melt structure and composition with a high degree of spatial and temporal resolution. However, the technique has not been fully exploited in studying fused salt electrolysis. The results of recent efforts in this laboratory both in the electrowinning of light metals and the electroplating of refractory metals are presented.

ELECTROWINNING OF ALUMINUM AND MAGNESIUM

Reasons for the loss of power efficiency in aluminum cells (2-4) and magnesium cells (5,6) have been discussed in the literature. Raman spectra of pure $MgCl_2$ and solutions of $MgCl_2$ in alkali chlorides have been measured

(7-13). In contrast, in the analogous aluminum chloride systems, spectra have been taken of $AlCl_3$ only in solution in alkali chlorides, as pure $AlCl_3$ sublimes without melting under an applied pressure of 1 atmosphere (14-18). Cryolite-based melts have also been the subject of investigation in previous studies (19-22).

In this laboratory the characteristics of laboratory-scale aluminum and magnesium cells have been investigated by spectroscopic and electrochemical techniques. The electrolytes were constituted to be representative of industrial conditions. Magnesium cells operated at a temperature of 750°C. The composition of the electrolyte was 11 wt % $MgCl_2$, 65 wt % NaCl, 18 wt % KCl, and 6 wt % $CaCl_2$, which is representative of anhydrous I.G. Farben chemistries widely used today. Aluminum cells operated at a temperature of 700°C. The composition of the electrolyte was 5 wt % $AlCl_3$, 42 wt % LiCl, and 53 wt % NaCl, which is representative of the Alcoa Smelting Process chemistry. A second aluminum cell operating at a temperature of 960°C with an electrolyte based on cryolite (Na_3AlF_6), which is representative of the Hall-Heroult chemistry, has also been constructed. In these cells the maximum current density was 2 A cm^{-2}.

As part of a study of the causes of poor power efficiency, these laboratory-scale electroreduction cells were studied by Raman spectroscopy. Commercially available laser Raman scattering instrumentation was adapted to permit *in situ* real-time investigation of melt chemistry and to establish the basis for "fast Raman" spectroelectrochemistry in these and other melt systems. The results of the Raman work were combined with those of cyclic voltammetry in an attempt to reveal the mechanisms and kinetic pathways that decrease power efficiency in aluminum and magnesium cells and also to understand the nature of such phenomena as metal fog, streamers, and melt coloration, all of which were observed in these laboratory-scale cells (13).

A detailed description of the Raman instrumentation and the laboratory-scale electrolysis cell can be found in previous reports (12,23). The preparation of anhydrous salts for electrolyte formulation has been described previously (12).

Figure 1 shows the Raman spectrum of aluminum chloride in its supporting electrolyte at a temperature of 610°C. The two traces correspond to dif-
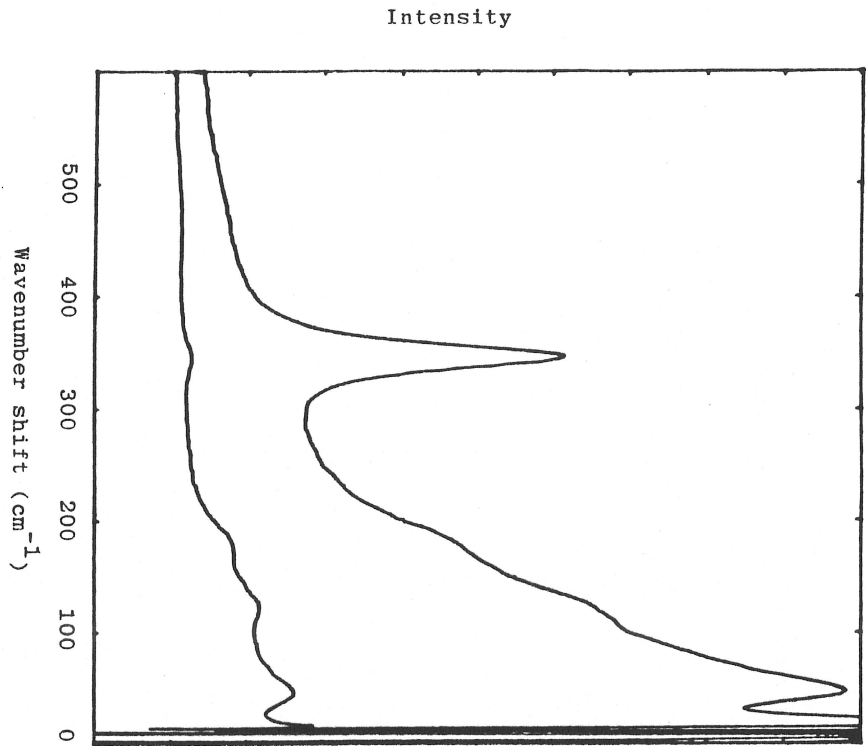
Intensity

Wavenumber shift (cm^{-1})

Figure 1. Raman spectrum of 10 wt % AlCl$_3$ - 40 wt % LiCl - 50 wt % NaCl. T = 610°C. λ = 514.5 nm.

Intensity

Wavenumber shift (cm^{-1})
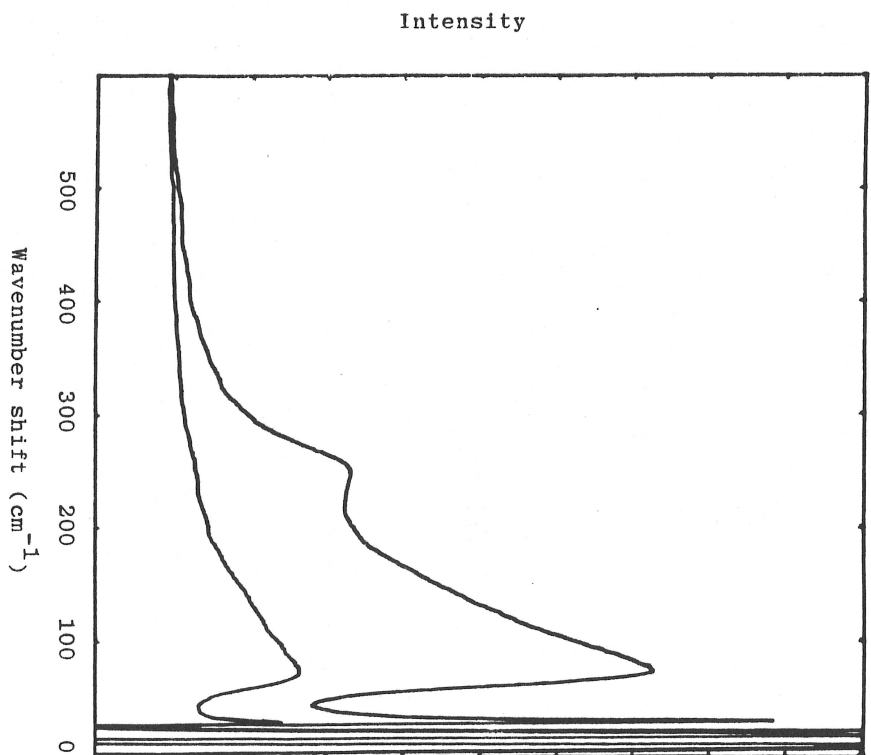
Figure 2. Raman spectrum of 11 wt % MgCl$_2$ - 6 wt % CaCl$_2$ - 18 wt % KCl - 65 wt % NaCl. T = 760°C. λ = 514.5 nm.

ferent polarization orientations. The plane of polarization of the exciting radiation was set by a rotator as either $^\perp$I or $^\parallel$I. The beam passed horizontally through the melt. The scattered radiation was collected at 90° and imaged onto the vertical entrance slit of the spectrometer while passing through a vertical polarization analyzer, $I_\perp$ always. Excitation was caused by radiation of wavelength 514.5 nm. Four distinct peaks have been identified: 125 cm^{-1}, 183 cm^{-1}, 349 cm^{-1}, and 483 cm^{-1}. The peak at 349 cm^{-1} is polarized; the others are depolarized. Such a pattern of peaks is indicative of tetrahedral coordination and suggests the presence of the tetrachloroaluminate complex, $AlCl_4^-$. The "peaks" around 75 cm^{-1} are instrumentation artifacts caused by the cutoff of the monochromator filter.

Figure 2 shows the Raman spectrum of magnesium chloride in its supporting electrolyte at a temperature of 750°C. Excitation was caused by radiation of wavelength 514.5 nm. Four distinct peaks have been identified: 107 cm^{-1}, 142 cm^{-1}, 249 cm^{-1}, and 351 cm^{-1}. The peak at 249 cm^{-1} is polarized; the others are depolarized. As was the case above with the aluminum chloride system, such a pattern is indicative of tetrahedral coordination and suggests the presence of the tetrachloromagnesate complex, $MgCl_4^{2-}$.

Figure 3 shows the Raman spectrum of pure molten cryolite at a temperature of 1015°C. Excitation was caused by radiation of wavelength 488.0 nm. The uppermost curve was taken without the use of the polarization analyzer. Two peaks have been identified: a strong polarized peak at 535 cm^{-1} and a weak depolarized peak at 390 cm^{-1}. These results are in agreement with those of Gilbert, Mamantov, and Begun, who concluded this to be evidence for the presence of the octahedrally coordinated hexafluoroaluminate complex, AlF_6^{3-} (21).

ELECTRODEPOSITION OF REFRACTORY METALS

The chlorides of the elements of groups 4, 5, and 6 react with alkali-metal chlorides to produce hexachlorocompounds. The volatile, covalently bonded refractory-metal chlorides exist in thermodynamically stable forms in these compounds, which, when dissolved in alkali-metal chloride melts, constitute potential electrolytes for the electrodeposition of the refractory metals. However, generation of coherent, smooth coatings is impaired in part
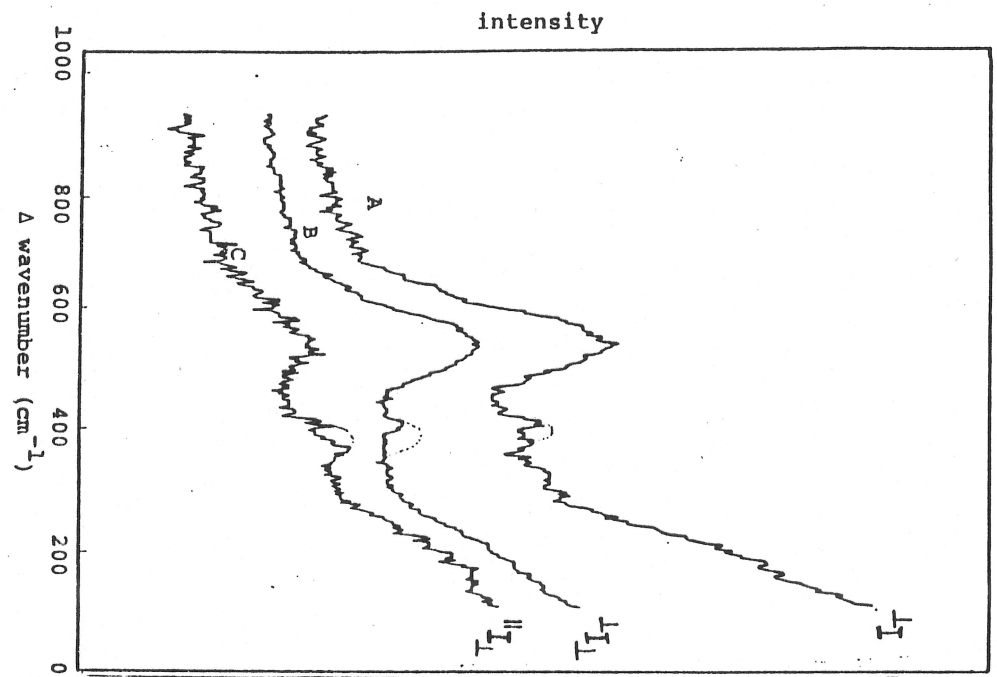
intensity

Figure 3. Raman spectrum of Greenland cryolite, Na_3AlF_6. T = 1015°C. λ = 488.0 nm.

INTENSITY
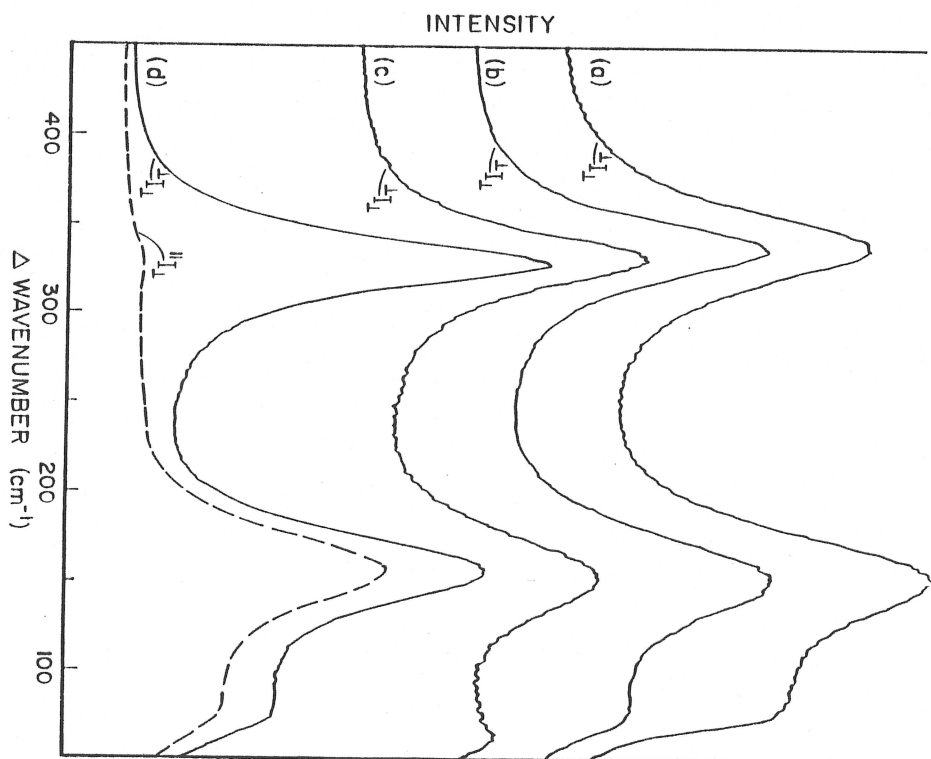
Figure 4. Raman spectra of alkali-metal hexachlorohafnates. (a) Li_2HfCl_6, T = 540°C; (b) Na_2HfCl_6, T = 685°C; (c) K_2HfCl_6, T = 850°C; (d) Cs_2HfCl_6, T = 870°C. λ = 514.5 nm.

by the formation of aliovalent species, which are difficult to identify during electrolysis. As a first step in determining whether Raman spectroscopy can be useful in analyzing melt chemistry during electroplating, Raman spectra of a variety of melts were measured in the A_2MCl_6 and $ANCl_6$ systems, where A is an alkali metal selected from Li, Na, K, and Cs, M is a group 4 metal selected from Zr and Hf, and N is a group 5 metal selected from Nb and Ta. The experiments have been described in the literature (23).

Figure 4 shows the Raman spectra of the family of alkali hexachlorohafnates at various temperatures on the range 540°C to 870°C. Excitation was caused by radiation of wavelength 514.5 nm. Spectra for both polarization orientations are reported only for Cs_2HfCl_6. While intensity is in arbitrary units, the same scale factor has been used in all traces. In each compound two distinct peaks have been identified: a strong polarized peak near 330 cm^{-1} and a strong depolarized peak near 155 cm^{-1}. The peaks appearing at 60 cm^{-1} are instrumentation artifacts caused by the cutoff of the monochromator filter. Such a pattern is indicative of octahedral coordination and suggests the presence of the hexachlorohafnate complex, $HfCl_6^{2-}$.

CONCLUSIONS

Raman spectroscopy has the potential to analyze melt chemistry with spatial and temporal resolution. This article has given examples of the use of Raman spectroscopy in the study of chemistries of importance in the electrowinning of light metals and the electrodeposition of refractory metals. It remains to be demonstrated that this information can be used in the optimization of these processes.

ACKNOWLEDGEMENT

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